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DUPLICATE

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## ENHANCING SPECTRAL DATA

### Technical Field

This invention relates to the enhancement of spectral  
5 data obtained from a spectrometer. The invention is  
described herein with reference to optical spectra. However,  
the invention can equally apply to any form of spectral  
data, such as data obtained from a mass spectrometer, for  
instance.

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### Background to the invention

Data obtained from a spectrometer comprises a series of  
peaks and troughs which correspond to species or elements  
present within a sample (often graphically represented as a  
15 graph of intensity versus wavelength, or frequency or  
energy). For the case of optical emission spectra, a sample  
can be excited using various known techniques. The  
excitation causes the energy of atoms to be elevated to a  
higher energy level. As the atoms in the excited sample  
20 relax or decay to a lower energy level of excitation,  
photons are emitted having a discrete wavelength, thereby  
producing a series of so-called spectral lines, each line  
corresponding to an energy transition. The energy, and hence  
wavelength, of the emitted photon is dependent on the energy

gap between the excited and relaxed state of the atom, amongst other things. The energy levels and the gap between excited and relaxed states are dependent on the atomic element being excited. Thus, it is possible to deduce the constituent elements in a sample by looking at the wavelengths of optical emissions from an excited sample.

Each spectral line has a width associated with it, which is usually measured as a full width half maximum (FWHM) value. The factors which govern the shape and the width of spectral lines hold for both emission and absorption processes. When two or more spectral lines are emitted from a sample with approximately the same wavelength, it can become difficult to resolve one spectral line from the other. This is particularly so if the lines are very close to one another, and/or the lines have a FWHM value which results in the lines significantly overlapping with one another. This can make it very difficult to ascertain the constituent elements in a sample. Such proximal spectral lines, which arise due to atomic energy level splitting are known as doublets or multiplets. Lines from different atomic species can be also proximal, leading to so-called spectral interferences. It is often advantageous to measure the intensity of some spectral line.

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This allows a measure of the concentration of the element in

the sample to be deduced, amongst other things. A relatively weak, or low intensity spectral line can become swamped by a relatively strong, or high intensity spectral line. This swamping effect can result in data of interest being masked.

5        Modern optical spectrometers use solid-state detectors, such as CCD (Charge Coupled Device) or CID (Charge Injected Device) which comprise at least one array of photo-detectors arranged downstream of a wavelength dispersing element and radiation source containing the excited sample. The array is  
10    mounted in the focal plane of the dispersing element. Because each detector has a finite physical width, each detector detects a band of wavelengths which is dependent on the width of each detector element, the dispersive power of the dispersing element, and the distance between the  
15    detector and dispersing element, among other factors. As a result, the resolving power of the spectrometer is limited by the number of detectors in the array and by the bandwidth of each detector.

      Spectral line detail can be averaged over the detector  
20    element bandwidth and the effect is more prominent if the detectors have insufficient resolution (that is, a resolving power lower than the optical resolution). Such averaging occurs when the detector element bandwidth is roughly of the same order of magnitude as the peak's FWHM. Averaging over



the pixel bandwidth results in information loss, for instance. This can lead to a loss of accuracy when on the accurate determining the line position.

Further, the intensity of spectral lines can be measured by integrating the detected radiation over a predetermined band-pass window consisting of one to several detector elements. The accuracy of such measurements is limited where the number of pixels in the band-pass window is relatively small because it is difficult to adjust precisely the integration limits. The integration limits are defined in order to control interference from nearby spectral lines; the more suitable-position of the integration limits allows more accurate and precise results to be obtained. However, this approach is not satisfactory when the number of pixels is insufficient. The position of the spectral lines on the array detector can drift over time, due to changes in the positions of optical components, often caused by temperature changes within the spectrometer structure, and/or due to optical emission source position variation caused by argon gas pressure changes within the source chamber, for example. With too few pixels or detector elements per spectral line, drift correction is more difficult and perhaps impossible. Drift correction must be set accurately to preserve the position of the lines and of

the integration limits. Higher pixel resolution can decrease errors on the determination of lines position when compensating for drift errors.

Greater resolution over a certain spectral range can be achieved by arranging a plurality of detectors in one spectrometer, where each array is arranged to detect a different part of the spectral range with respect to the other arrays. A possible optical arrangement for a spectrometer of this kind is shown in figure 1, which shows the spectrometer 10 in highly schematic form. The excited sample S emits radiation 12 which comprises many spectral lines. Optical objectives 14, 16 and 18 respectively, each sample a portion of the radiation into the spectrometer. The radiation passes through entrance slits 20, 22, and 24 respectively. The sampled radiation then impinges on wavelength dispersing elements 26, 28 and 30 respectively. In this arrangement, the elements are reflection gratings, known in the spectrometer art although other types of dispersing elements can be used. Each grating determines the wavelength of radiation which is reflected onto detector arrays 32, 34 and 36 respectively, disposed in the focal plane of the grating 26, 28 and 30 respectively.

The arrangement shown in figure 1 is similar to that of the ARL-QUANTRIS spectrometer manufactured by Thermo

Electron Corporation. The detector arrays are arranged to detect wide spectral areas containing many emission lines. The detectors are solid-state devices containing a great number of pixels on a substrate - typically 8640 pixels per array. On this particular instrument, an array is large enough so all spectral lines of interest in a specified wavelength range fall onto the array. The array must also consist of sufficient pixels so that each line is recorded with sufficient digital resolution (each detector element producing a "digit" the value of which is representative of the intensity of light detected by the element). This requires a great many pixels, usually more than 20 pixels per nanometre wavelength.

We use the term 'digital resolution' to describe the resolution of the signal limited by the wavelength or frequency interval between two discrete consecutive values. In a raw spectrum, the digital resolution is thus limited by the bandwidth of the pixel and (for some detectors) the dead space between pixels (for the CCD on ARL QUANTRIS this dead space is zero). We use the term 'spectral resolution' to describe the optical-resolution limited of the optical components prior to the detector, which may include an entrance slit and the dispersive element, for example. These two resolution limits are combined when the spectrum is

measured, and the combination of the two results in a resolution lower than each individually resolution.

Presently, arrays are not readily available with sufficient numbers of pixels so that recording a full spectrum allows each line to be represented with sufficient digital resolution. Resolution can be improved by physically splitting the spectrum into several portions, each with an array detector. This however does not sufficiently resolve all the spectral lines of interest. Other examples of instrumentation with limited digital resolution are the ARL QUANTODESK and ARL EASYTEST, both also manufactured by Thermo Electron Corporation. These instruments have a reduced spectral domain in comparison to ARL QUANTRIS and a single array detector.

On the ARL QUANTRIS, each portion of the spectrometer usually requires a separate dispersive element 26, 28, 30, and a separate optical path from the sample to each dispersing element, as shown in the arrangement of Figure 1. The digital resolution can also be limited because the instrument designer wishes to incorporate the ability of measuring the whole spectrum in an instrument and/or must compromise between limits of digital resolution of the spectrum due to the number of pixels covering each radiated line, detector cost, and cost and complexity of the

spectrometer optics. Under other circumstances, limited digital resolution may be deliberately chosen to save time. This is the case in sequential spectroscopy techniques, where sampling every second point would allow time saving by a factor of 2.

A limited number of pixels per optical line results in an uncertainty in the position of the centre and on the maximum intensity of the line. The position of the centre of the line is important for drift correction and for correctly determining the element that caused its emission, and therefore for correctly analysing the sample material. As described above, the intensity of the line is used for quantification of emitting element specific concentration. Insufficient digital resolution can also be critical when dealing with overlapping or interfering lines. Such problems can also make the process of calibrating the spectrometer more difficult.

Referring to figure 2, a typical spectrum 50 recorded with the ARL QUANTRIS spectrometer is shown. The spectrum is a graphical representation of the recorded radiation intensity 52 (in arbitrary units) as a function of wavelength 54 (measured in nanometers). The sample used to create this spectrum is composed of pure iron. As can be

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seen, the spectrum is very complex with more than 6000 lines.

spectral lines being visible on a 8640 pixel CCD array. A spectrum from a multi-element sample can be more complex still, depending on the concentration levels of the elements that compose the sample.

5        Figure 3 shows a portion of the spectrum of figure 2, which is presented as a bar graph 60 of the signal detected by each individual detector element. The graph clearly shows that the resolution of the detected wavelengths is limited by the size or resolving power of the detector array. Each  
10    detector element effectively has a width over which it integrates the radiation incident upon it, creating a small wavelength band-pass. The size of this band pass (usually quoted in picometers wavelength) depends, amongst other things, on the physical size of the pixel detector, as  
15    discussed above.

Several line types appear in figure 3: a single line 62 in the middle, with a FWHM (Full Width at Half Maximum) of roughly 2 - 3 pixels or detector elements; two overlapped lines, 64 and 66 respectively, to the left; and an  
20    unresolved group of peaks 68 to the right. The single line 62 is not centered on a pixel so that it is difficult to determine accurately where the centre of the line is. Not knowing the central position of the line, together with  
having too few digital measurements across the line, makes

calculating the intensity of the line difficult, and hence deducing the quantity of the element that produced the line is also difficult.

The spectrum represented in Figure 2 and 3 is a line spectrum because the dispersing system produces, for each wavelength, an image of an entrance slit. The slit is arranged to be narrow in the dispersing plane to give adequate spectral resolution, and tall in the perpendicular plane to increase the amount of radiation transmitted to the detector. The FWHM of each individual wavelength, expressed in pixels, depends on the combination of the entrance slit width, the reciprocal dispersion of the dispersing element (grating) and the number of physical pixels on the CCD detector/array. Thus, it is essential to have sufficient resolution to be able to determine elemental compositions with spectra as complex as that shown in Figures 2 and 3.

Furthermore, it is important to have high transmission to be able to measure low concentrations of elements within the sample material. Transmission can be improved by enlarging the entrance slit (but this degrades resolving power). However to maintain resolution, the dispersion of the spectrometer must also then be increased. Increasing the dispersion requires a physically larger instrument. This places impractical constraints on the spectrometer design...

If the entrance slit is enlarged and the dispersion increased to maintain resolution, the image of a single line at the detector is also increased. However, for the same size of detector array, there are more pixels per line, increasing the digital resolution, as desired.

In the example of the ARL QUANTRIS, the CCD detector used for each spectrograph have 8640 pixels in a line across the focal plane, each pixel having a physical dimension of  $7.0\mu\text{m} \times 9.8\mu\text{m}$ . The wavelength coverage of each spectrograph and the band pass for each pixel are as follows:

- Spectrograph 1: 129-200nm, 8.22pm (Pico meter)/pixel,
- Spectrograph 2: 200-410nm, 24.31pm/pixel, and
- Spectrograph 3: 410-780nm, 42.82pm/pixel.

This optical arrangement leads to a FWHM of the analytical lines of:

- Spectrograph 1: 4 - 6 pixels/FWHM
- Spectrograph 2: 2 - 3.5 pixels/FWHM
- Spectrograph 3: 2 - 3.5 pixels/FWHM.

The variability in pixels/FWHM is due to the FWHM changing due to effects related to physical phenomena in the discharge plasma, which are mainly matrix type dependant. For instance, the emission lines in an Al matrix are wider than those in a Fe matrix.



Another example of instrumentation on which the invention can be applied is the ARL QUANTODESK instrument. The optics of this instrument has one spectrograph in the wavelength range 170-410 nm and the CCD detector has 8044  
5 pixels.

There are several requirements which are constrained by the digital, or pixel, resolution. Specifically, the accuracy of the tabulated wavelengths in the line atlases or databases is less than 1pm (Pico meter).

10 With the ARL QUANTRIS instrument, the confidence limit in peak positioning is half of a pixel (i.e. about 4 pm in the case of spectrograph 1), which is not sufficient. In order to positively identify a line, a higher digital resolution than the examples given above is needed.

15 Present methods which might increase the peak positioning accuracy, in most of the cases, use fitting techniques. Fitting techniques, such as gaussian, Lorentzian and polynomial (parabolic) fits have proved unsatisfactory mainly because these techniques are not able to provide  
20 sufficient accuracy of the peak wavelength of a spectral line. Inaccuracy on the peak wavelength is typically observed when the peak shape is not ideal, for instance asymmetrical or due to overlap with one or several other

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spectral peaks. Also, such techniques do not allow accurate

measurement of the peak intensity, and hence element concentration in the sample. Using such fitting techniques to calculate spectral line characteristics (such as line maximum position, maximum intensity and peak width, for instance) requires the raw data to ideally have a perfect shape, that is the line should be symmetrical, free from interference (which might be caused by proximate spectral lines causing overlap), and have a profile corresponding to the fitting curve (Gaussian profile if a Gaussian fit is being used) for an accurate fit to be performed. It is highly unlikely that these conditions will ever be realised in real spectral data, for instance distortions in line shape may occur due to optical or instrument aberrations, spectral line overlap, doublet interferences for example. As a result, improvement of the spectral line shape is often not satisfactory using these known techniques.

The problems outlined above limit the performance of optical emission spectrometers, as well as other kinds of spectrometers, for a given cost.

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#### Summary of the Invention

It is desirable to increase the digital resolution in an attempt to resolve the problems discussed above.

Additional improvements to spectra are also desirable, such

as improvements to the signal to noise ratio, and signal interpolation.

The present invention aims to ameliorate the problems described above by providing a method of enhancing spectral data, said data comprising M discrete intensity values within a range of wavelength values,

said method comprising:

- a) applying a first function to the spectral data to obtain an inverse transform of the spectrum,
- 10      b) zero-filling said inverse transform, and
- c) applying a second function to the zero-filled inverse transform to obtain a spectrum comprising N discrete intensity values within said range of wavelength values, and wherein  $N > M$ .

15      The first function can be a Fourier transform function which produces an inverse Fourier transform of the spectral data. Because the spectral data is a wavelength-spectrum then the inverse transform is of a time-domain interferogram type. In other words, the spectrum can be transformed into a time-domain-like acquisition by inverse Fourier transform or

20      any transform producing a comparable effect.

Preferably, the first function is an inverse Fourier transform (IFT) that transforms the acquired wavelength

spectral data into a time-domain-like acquisition, hereafter

referred to as pseudo-time domain signal or interferogram.

This interferogram is comparable to acquired signals from known Fourier transform (FT) instruments (for instance FT-NMR or FT-IR). The second transform stage is a transform

5 function, the reciprocal of the first function, which transforms the signal back to the spectral representation of the signal. Other functions (and their reciprocal functions) might also be used to produce similar transformations (for instance z-transform).

10 Preferably, the invention further comprises the step of: i) apodizing said zero-filled inverse transform prior to applying the second function. The second function can be applied to the apodized zero-filled inverse transform. Apodization can be used to improve signal-to-noise ratios of  
15 the enhanced data.

Furthermore, when the inverse transform is zero-filled

by a factor  $Z$ ,  $N$  is  $Z$  times greater than  $M$ . Preferably,  $Z$

should be in the range of 2 to 10. When  $Z$  is greater than

10, there is a burden on computing the enhanced data. Of

20 course, as computational methods advance, values of  $Z > 10$  may be used to great effect. The ceiling value for  $Z$  of 10 is not considered limiting, and higher values might be used without leaving the scope of the invention.

The present invention also provides a computer programme, which when run on a computer, carries out the method steps described above.

Furthermore, the present invention provides a Spectral data enhancing apparatus comprising, a spectrometer for obtaining spectral data which has M discrete intensity values within a range of wavelength values, first means for applying a first function to the spectral data to obtain an inverse transform of the spectrum, second means for zero-filling said inverse transform, and third means for applying a second function to the zero-filled inverse transform to obtain a spectrum comprising N discrete intensity values within said range of values, and wherein  $N > M$ .

Embodiments of the present invention improve spectral details and resolution, allow the use of cheaper CCDs (possibly with fewer pixels than is presently required for necessary resolving powers) and/or to reduce the time taken to obtain accurate spectra. The time saving is particularly beneficial in sequential (scan) techniques.

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#### Description of the drawings

An embodiment of the present invention is now described, by way of example, with reference to the following drawing, in which:

Figure 1 shows a schematic diagram of a known optical emission spectrometer;

Figure 2 shows a portion of an optical emission line spectrum for Fe;

5     Figure 3 shows a portion of the spectrum of figure 2;

Figure 4 shows the data from figure 3 after shifted IFFT function has been imposed on the data;

Figure 5 shows raw data obtained from an optical emission spectrometer;

10     Figure 6 shows the data of figure 5 once it has been enhanced according to a first embodiment of the present invention;

Figure 7 shows the data of figure 5 once it has been enhanced according to another embodiment of the present

15     invention;

Figure 8 shows the data of figure 5 once it has been enhanced according to a further embodiment of the present invention;

Figure 9 shows another data set representing raw  
20     spectral data;

Figure 10 and 11 show the data-set of figure 9 after linear interpolation has been performed;

Figure 12 and 13 show the data set of figure 9 after functions according embodiments of the invention have been performed;

Figure 14 is a plot of the data of figure 11 and 13  
5 superimposed on the same graph;

Figure 15 is a plot showing various different apodization functions which can be applied to data;

Figure 16 is a plot of raw data obtained from a pure aluminium sample;

10 Figure 17 shows the data of figure 16 after a method embodying the present invention has been applied without apodization; and

Figure 18 shows the data of figure 16 after a method embodying the present invention has been applied with  
15 apodization.

#### Detailed description of embodiments of the present invention

An embodiment of the present invention comprises a method of manipulating digitised spectral data which can  
20 produce a resultant spectrum that more accurately resembles the physical spectrum emitted from the sample. In other words, the enhanced/manipulated spectral data more closely correlates with the actual spectrum emitted by the sample.

The method comprises steps, some of which are not essential, which should be carried out on the digital spectral data, as follows.

Step 1: To a raw spectrum (spectral or frequency-  
5 domain) defined by a set of  $2^m$  pixels (where  $m$  is an integer number), apply an Inverse Fast Fourier Transform (IFFT).  $2^m$  data points are required for applying Inverse Fast Fourier Transform algorithm. (Shifted IFFT provides result as a symmetrical pseudo-interferogram; all computations are more  
10 elegant due to the symmetry). An "interferogram" type data set is obtained, in a 'pseudo'- time domain. The interferogram has  $M = 2^m$  (un-shifted IFFT) or  $2^m+1$  (shifted IFFT) data points; depending on the way the dataset is handled. Such an interferogram 80 is shown in Figure 4. In  
15 this case, it has  $2m+1$  data points, it is symmetrical about time  $t=0$  and has the time scale normalized to 1 seconds, from  $-0.5$  to  $+0.5$  seconds.

Step 2: zero-filling the interferogram thus adding  
( $2^{n-m}-1$ )  $\cdot 2^m$  data points with intensity equal to zero. This  
20 increases the number of data points to  $2^n+1$  where  $n>m$ . The number  $2^{(n-m)}$  gives the degree of zero filling. Zero-filling is a technique by which zero values are added (symmetrically only for the shifted IFFT) to the real and the imaginary part of the IFFT for the new data points. In other words,



the IFFT data between -0.5 and 0.5 on the pseudo time scale remains unchanged and data with a value of zero is added to the IFFT between values of -1.0 to -0.5 and 0.5 to 1 (in this case where the time scale is enlarged by a factor of 2, 5 the degree of zero-filling is 2).

Step 3: (optional, non-essential step) apply apodization to the interferogram. Apodization is a multiplication of the imaginary and real part of the IFFT interferogram with a selected function in order to improve 10 either the signal-to-noise ratio (equivalent to smoothing), to the detriment of resolution, or to improve spectral resolution to the detriment of the signal-to-noise ratio. Examples of apodization are discussed below.

Step 4: apply a Fast Fourier Transform (FFT) to the 15 results of steps 2 (or step 3, if used). The obtained spectrum has  $2^n$  points.

As an example, Figures 5, 6, 7 and 8 show the effect of zero-filling to various degrees on an inverse Fourier transform of a raw optical emission spectrum, followed by 20 the FFT back to the wavelength domain. No apodization (i.e. step 3 outlined above has not been performed) has been performed on the data in the example shown in these figures. The raw spectrum was recorded with spectrograph 2 of ARL

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QUANTRIS using a CrNi steel sample to produce a spectrum.

Figure 5 shows the raw data 90, obtained from the spectrometer, plotted as a function of pixel number against an arbitrary intensity value; the pixel-limited digital resolution is evident. Three examples of zero-filling are presented in figures 6, 7 and 8, where the factor of zero-filling used is 2, 4 and 8 respectively.

As can be seen, zero-filling alone does not change spectral resolution, but it does increase the digital resolution, it also restores the natural shape of the peaks (the manipulated data peaks having a "less-digitised look") and unveils minor details previously hidden, such as the peak indicated by numeral 92 in figures 6, 7 and 8 which is not present in the raw data. Furthermore, the raw data shows a spectral domain 94 which comprises two adjacent spectral peaks 96, 98 of different intensity. However, the same domain 100 in the manipulated/zero-filled data of figures 6, 7 or 8 shows two peaks with substantially the same intensity.

The resultant spectrum can be analysed to determine the peak position with an accuracy and precision which was previously not readily possible. Integration limits can be set with far greater precision (up to a factor 8 in the example shown in figure 8). Drift compensation can also be more precisely applied. This technique reduces the

correction scale unit down to a logical pixel instead of a physical pixel width.

5     Comparison of data fitted using an embodiment of the present invention with known techniques.

A comparison of data manipulated using an embodiment of the present invention with the technique of linear interpolation is now presented. Figure 9 shows some raw  
10     spectral data 100 presented as a histogram chart. The data comprises of a selection of twenty-six data points plotted along the x-axis, each having different intensities which are represented by the height of each bar in the histogram, and which are plotted along the y-axis. It can be seen that  
15     the spectrum comprises two singlet peaks 102 and 104, and a doublet 106. The first peak appears to have a FWHM value of between one and three pixel widths - it is certainly not possible to give an accurate estimation of the peak's FWHM value. Likewise with the other peaks shown in the spectrum.

20     Referring to Figures 10 and 11, a plot of the spectral data 100 of figure 9 is shown after the data has been subjected to linear interpolation of a fourth and eighth degree respectively. Briefly, a straight line is plotted

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between two adjacent data points by plotting a number of

contrived data points between real data points. If linear interpolation is carried out to two degrees, then two contrived data points are plotted between two adjacent real data points. Likewise if linear interpolation is carried out  
5 the eighth degree, then eight contrived data points are plotted between two adjacent real data points.

The results linear interpolation plot 110 shown in figures 10 and 11 are plotted as histogram charts. It can be seen that linear interpolation only goes a small way to  
10 improving the raw data. For instance, it is still difficult to ascertain exactly the centre of the second peak 114, or the centre of the second doublet peak 118. The situation is not improved by using a higher power linear interpolation plot 120 as shown in figure 11. By increasing the degree of  
15 interpolation it can be seen (from a comparison of figures 10 and 11) that no great benefit is yielded for someone trying to determine the centre of peak 124, etc.: The centre of peak 124 appears to be in exactly the same position as the centre of peak 114.

20 Referring now to figures 12 and 13, a plot of the spectral data 100 of figure 9 is shown after the data has been subjected to manipulation according to an embodiment of the present invention of a fourth and eighth degree respectively without apodization. Once again, figures 12 and

13 show a selection of a spectrum after manipulating all 8640 pixels in the spectrum, and not just the 26 pixels displayed.

From the resultant manipulated data shown in figure 12 and figure 13, it can be seen that it is much easier to discern details in the spectrum which were not otherwise obvious from either the raw data or the data which has undergone linear interpolation. For instance the centre of peak 134 and 144 can now be easily determined, compared to inadequate centre measurement of peaks 104, 114 or 124. Also, the shape of the doublet 136 and 146 is much better defined with respect to the raw data and data having linear interpolation performed thereon. Interestingly, features in the zero-filled data appear which were not present obviously apparent from the raw data or linear interpolated data. For instance, the peak indicated by numerals 137 and 147 is not entirely apparent in either the raw data or data on which linear interpolation has been performed.

Referring now to figure 14, a direct comparison of the plots shown in figures 11 and 13 is made. Here, the data from each of the respective data points is shown as a line plot, rather than a histogram. This makes the comparison easier to visualise. The data from figure 11 (that is, the linear interpolation to an eighth degree data) is indicated

by line 150 (individual intensities represented by diamonds  
on line 150). The data from figure 13 (that is the zero-  
filled data according to an embodiment of the present  
invention) is indicated by line 152 (individual intensities  
5 represented by circles on line 152).

The singlet peak 162 on the left hand side of the  
spectrum shows relatively good correlation between the zero  
filled data and the linear interpolation data. The FWHM of  
both sets of data are similar and both sets of data show  
10 good correlation for the predicted centre wavelength of this  
peak. Also, the intensity of the peak 162 is similar for the  
linear interpolated and zero-filled data.

However, there are large differences in the  
characteristics of other peaks in the data which are readily  
15 apparent. For instance, the intensity of the peak 164 varies  
considerably between the two data sets. Likewise there is  
little correlation between the data sets with regards to the  
overall shape of the doublet 166, particularly the right-  
hand peak of the doublet. Also, the centre of the peaks is  
20 much more clear from the zero-filled data, particularly for  
the 164 peak. It is not at all clear from the linear  
interpolated data exactly where the centre of peak 164 lies.  
It would appear to be anywhere between pixel number 19 to 20

(on the x-axis). However, the zero-filled data shows a clear discernable peak at one value.

### Apodization

5        Apodization is a known method of further manipulating data to increase signal to noise ratio, or to increase resolution. Essentially, apodization comprises imposing a function on the real and imaginary data of a time-domain signal. Depending on the apodization function chosen, the  
10    resultant data can be further enhanced when it is transformed back into the wavelength domain.

Figure 15 shows various apodization functions: a so-called cosine square 180, a so-called shifted sine-bell 182 and a Hamming function 184. The cosine square function  
15    almost fits the signal 190 envelope which looks as a function centred at maximum decaying monotonously towards the ends. The further the signal is from the centre of the graph, the more the intensity is reduced by multiplying by the function. The resultant signal envelope has a faster  
20    decay which corresponds in the spectral domain to a broader FWHM. Noise being constant over the interferogram, the part of the interferogram with the worst signal to noise ratio is given less weight. In other words, the signal to noise ratio

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is improved at the expense of spectral resolution. Other

functions have a monotonous decay and perform in a similar way as the cosine square function, for instance an exponential. A variety of other known functions can be used to improve the resolution, for instance a shifted sine-bell  
5 or a hamming function. Usually these functions put less weight on the part of the interferogram 190 about and close to time=0s, than on the intermediate parts, for example, about and close to times= $\pm 0.10 - 0.30$ s.

Figure 16, 17 and 18 show the effects of zero-filling  
10 only and of apodization on a zero-filled spectrum. An Inverse Fast Fourier Transform is applied to the raw optical emission spectrum 200 (Figure 16), followed by zero-filling (Figure 17) and by zero-filling and apodization (Figure 18). Finally a Fast Fourier transform returns the data to the  
15 wavelength domain. In this example a pure Al sample spectrum is used. Using as an apodization function  $\cos(t)^2$  (so-called square cosine bell, 180 in figure 15) where  $t$  is the pseudo time, a smoothing effect is obtained, as can be seen by comparing figures 17 and 18. This smoothing is important for  
20 evaluating background regions and improving the signal-to-noise ratio for data at low concentration levels. It can be seen that the smoothing has improved the signal-to-noise ratio of the data set, but at the expense of spectral resolution; the line widths have increased. Other



apodization functions are available that also improve the signal-to-noise ratio in this way. Normally these are functions that make the envelope of the pseudo time signal shorter.

5       Improvements to the digital resolution are only worthwhile if the spectral resolution is greater than the digital resolution. Apodisation technique can be used to improve digital resolution in cases where the pseudo-time domain data is truncated (i.e. has a significant intensity  
10   at the extremities). In such cases, after zero filling; Fourier transforming the signal leads to artefacts in the structure of the peaks or lines. To avoid this, truncated signals in the pseudo-time domain can be apodized to more smoothly take the signal to zero. This apodization itself  
15   leads to line or peak broadening. To avoid this, linear prediction is applied to generate the additional data points required to take the pseudo-time signal to zero, without introducing the line broadening effects of the apodization function.

20       The method of the present invention is in a neighbouring field to methods used in other Fourier Transform spectroscopy techniques, such as FT-NMR, FT-IR, FT-Raman and FT-ICR. These Fourier Transform techniques are known. For these techniques the application of zero-filling

and apodization are well-developed computation steps, which are followed by a Fourier Transform to obtain a spectrum.

For the present invention, the inventors have realised that transforming a measured wavelength-domain (inverse  
5 frequency-domain) spectrum into a pseudo-time domain allows the use of data manipulation techniques, even though they had originally been developed for use with time-domain data sets. As a result, embodiments of the present invention use two Fourier Transform stages. The first is an inverse  
10 transform. This can be described as 'forced', or 'unnatural', as it produces an interferogram in the pseudo-time domain (which might be considered analogous to any directly measured interferogram obtained by the Fourier Transform spectroscopy techniques mentioned above).

15 Known spectroscopy techniques record a spectrum in the time domain directly. However, in embodiments of the present invention, a spectrum is measured in the wavelength or frequency domain, and an inverse Fourier Transform is applied to the data to give a spectrum in the pseudo-time  
20 domain. The zero-filling, apodization and the second Fourier Transform are then applied to obtain an enhanced spectrum in the inverse frequency (wavelength) domain.

Besides application to the field of optical emission spectrometry, methods embodying the present invention can be

applied to other spectrometers which produce intensity versus wavelength measurements, such as ICP-OES, ED-XRF and WD-XRF. It can also be applied to spectrometers where intensity versus mass measurements are produced, such as  
5 ICP-MS, GD-MS, organic MS-MS or triple quadrupole techniques using, for example, electro-spray sources.

In addition, imaging spectroscopes such as ICP-CID spectra (with a bi-dimensional FFT processing) can be treated by methods of this present invention.

10 Furthermore, it can be applied to spectra that have been recorded by sequential spectrometers. In such cases, it can save important scanning time (and costs) by increasing the scan step size by a factor of two or four, without prejudice to the final spectrum.

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CLAIMS

1. A method of enhancing spectral data, said data comprising M discrete intensity values within a range of wavelength or frequency values,

said method comprising:

a) applying a first function to the spectral data to obtain an inverse transform of the spectrum,

b) zero-filling said inverse transform, and

10 c) applying a second function to the zero-filled inverse transform to obtain a spectrum comprising N discrete intensity values within said range of wavelength or frequency values, wherein  $N > M$ .

15 2. A method according to claim 1, further comprising the step of:

i) apodizing said inverse transform, before zero-filling and applying the second function.

20 3. A method according to claim 2, wherein the second function is applied to the apodized zero-filled inverse transform.

4. A method according to claim 1 or 2, wherein when the inverse transform is zero-filled by a factor Z, N is Z times greater than M.

5 5. A method according to any preceding claim, wherein the spectral data comprises an atomic emission spectrum.

6. A method according to claim 1, 2 or 5, wherein the spectral data is in the ultra-violet, visible and/or  
10 infrared domain.

7. A method according to any preceding claim, wherein the first function is a Fourier Transform function and second function is an inverse Fourier Transform function.

15

8. A method according to any preceding claim, wherein the spectral data and the spectrum are a frequency domain spectrum.

20 9. A computer programme, which when run on a computer, carries out the method according to any preceding claim.

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10. Spectral data enhancing apparatus comprising,  
a spectrometer for obtaining spectral data which has M  
discrete intensity values within a range of wavelength or  
frequency values,

5 first means for applying a first function to the  
spectral data to obtain an inverse transform of the  
spectrum,

second means for zero-filling said inverse transform,  
and

10 third means for applying a second function to the zero-  
filled inverse transform to obtain a spectrum comprising N  
discrete intensity values within said range of wavelength or  
frequency values, and wherein  $N > M$ .

15

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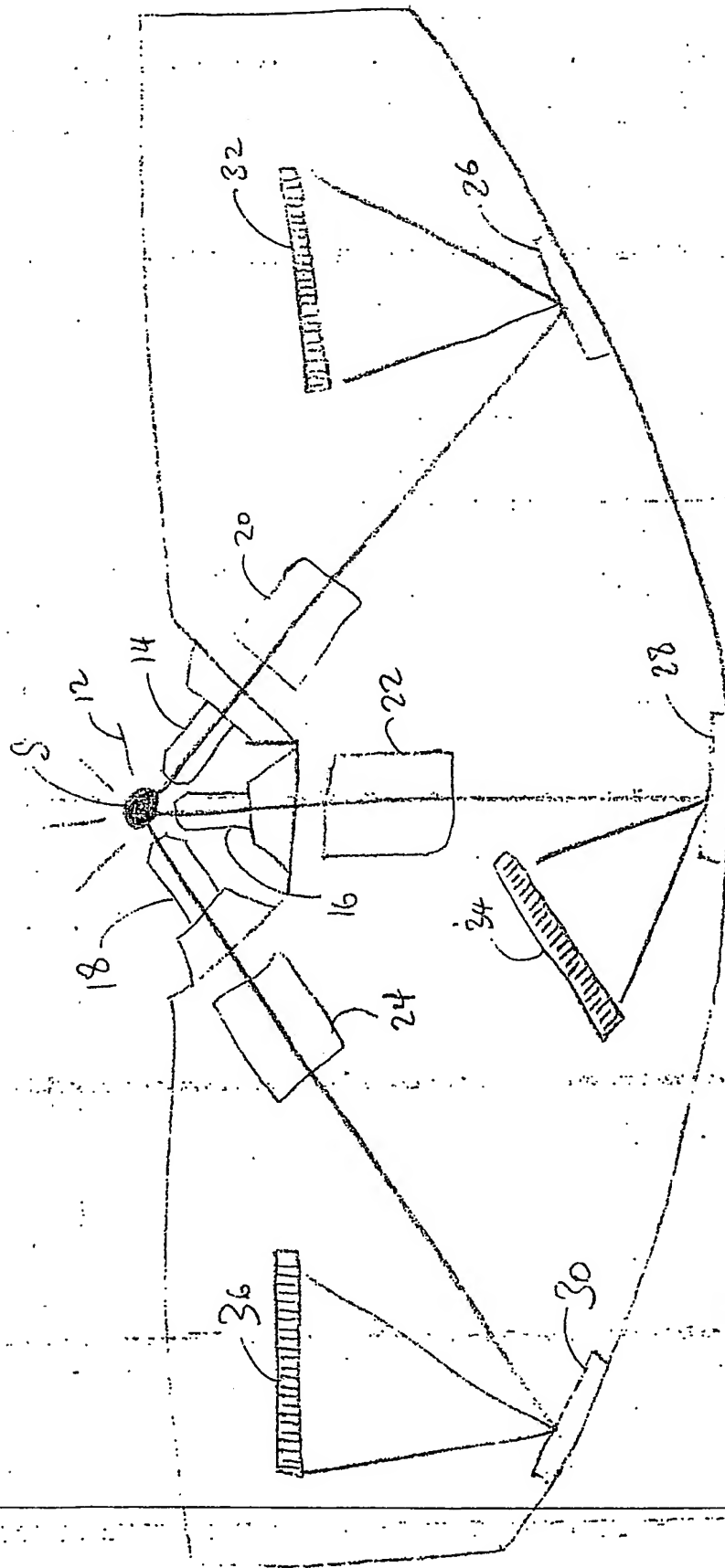


Fig 1.

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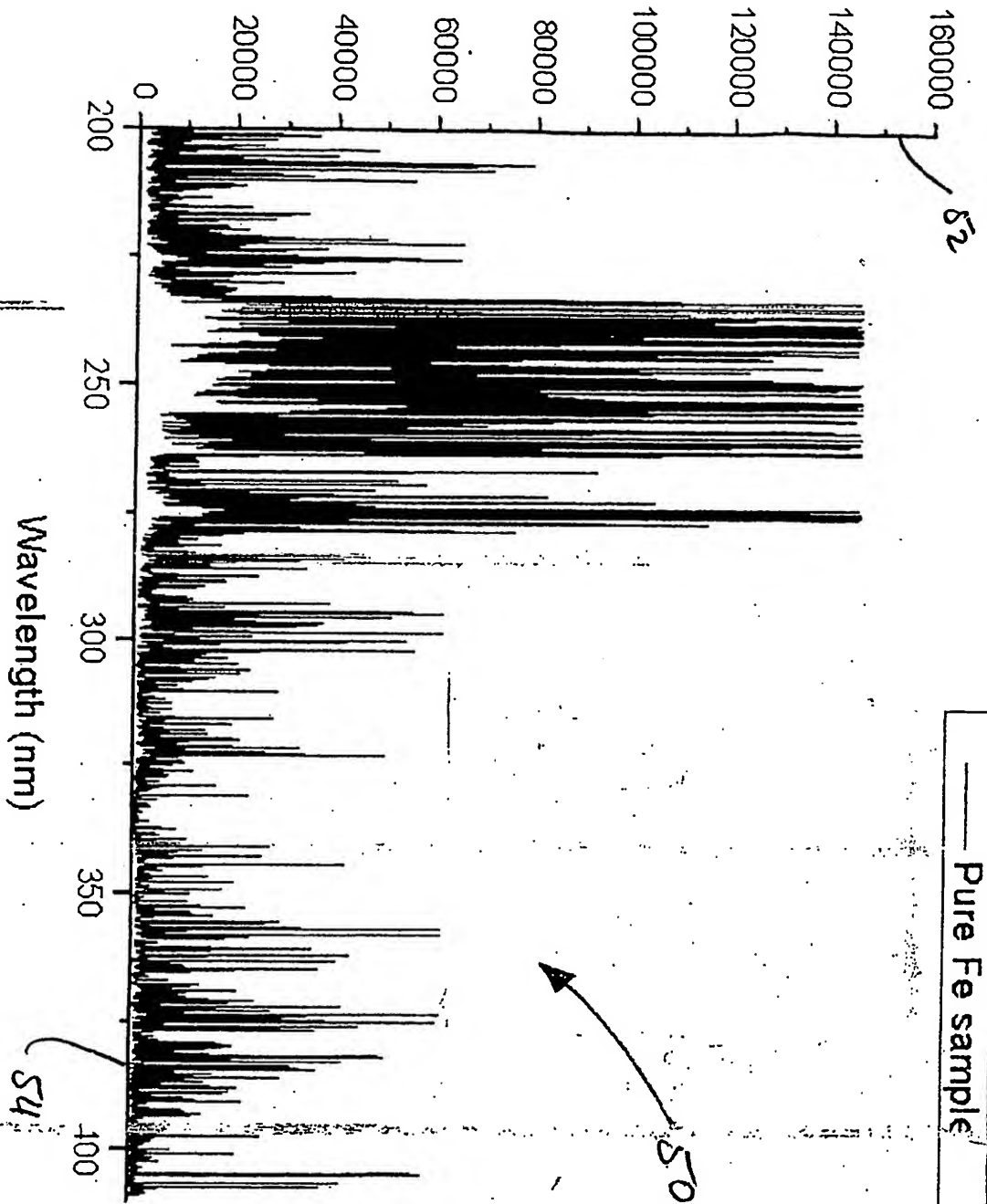


fig 2



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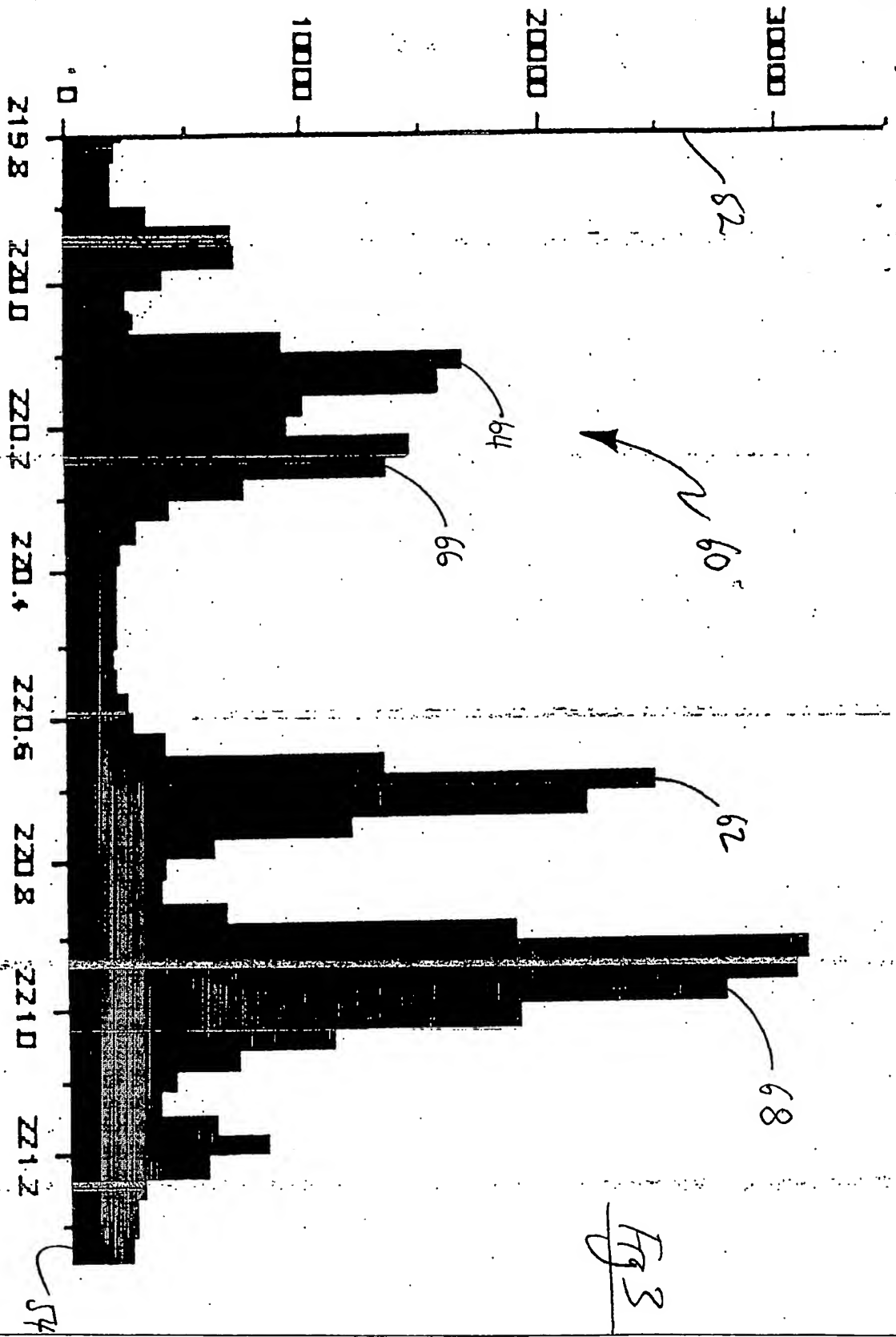


Fig 3

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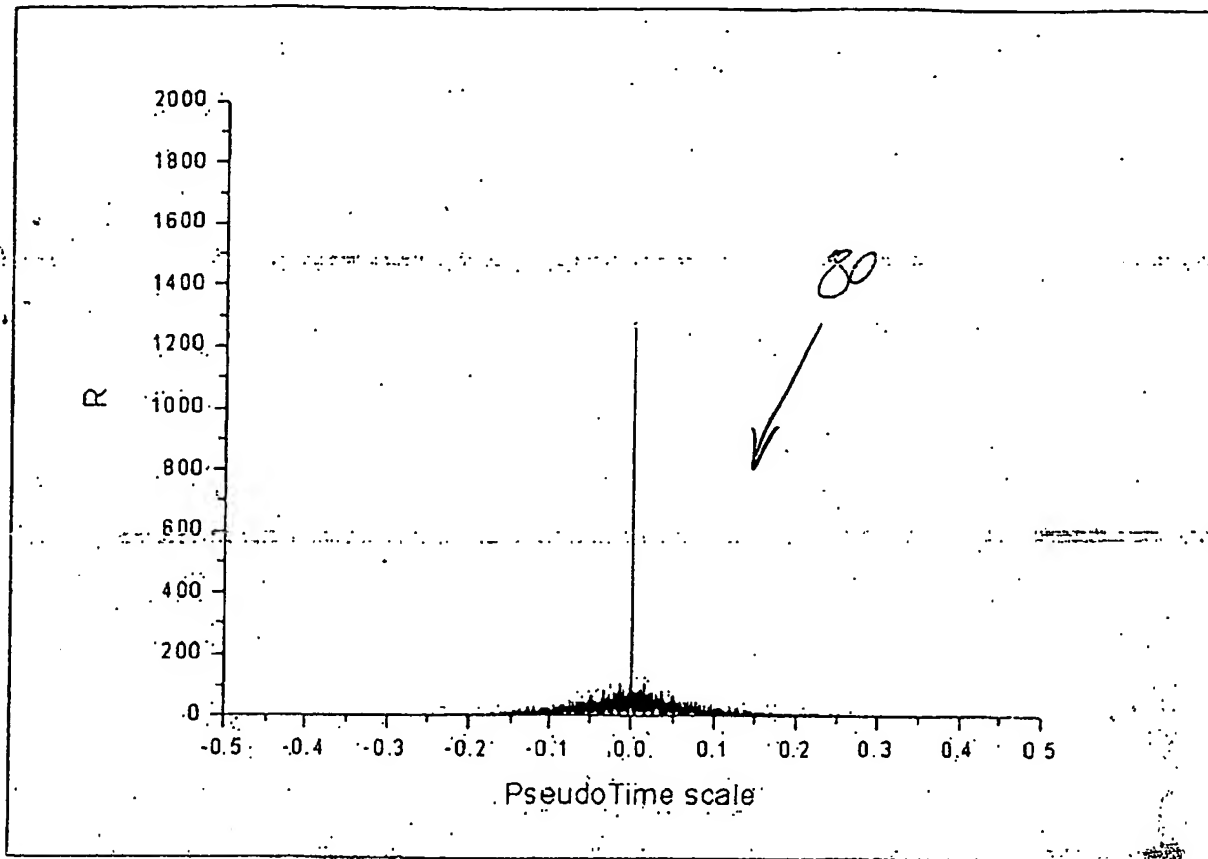


Fig 4.

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Fig 5

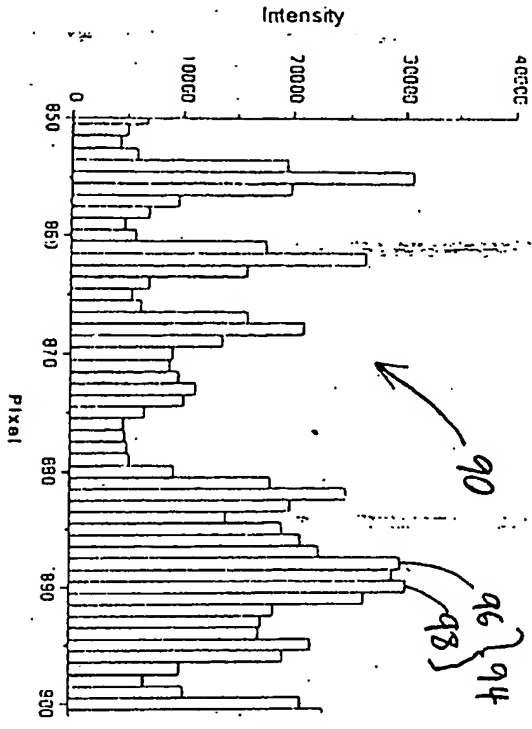


Fig 7

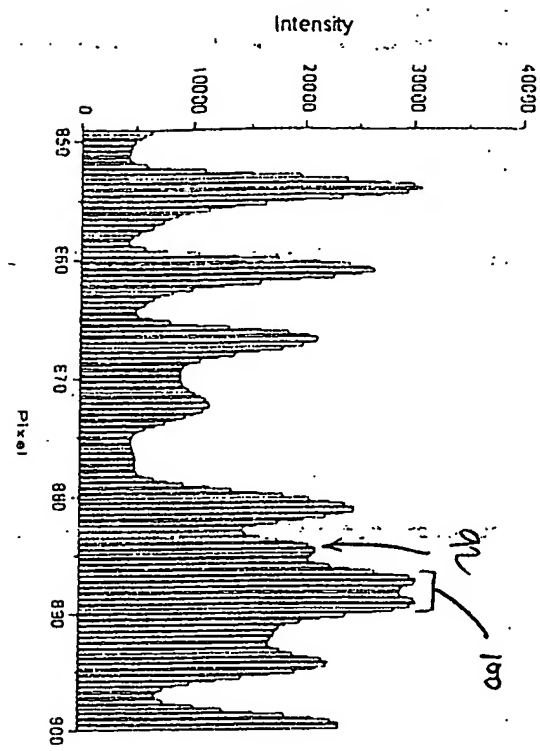


Fig 6

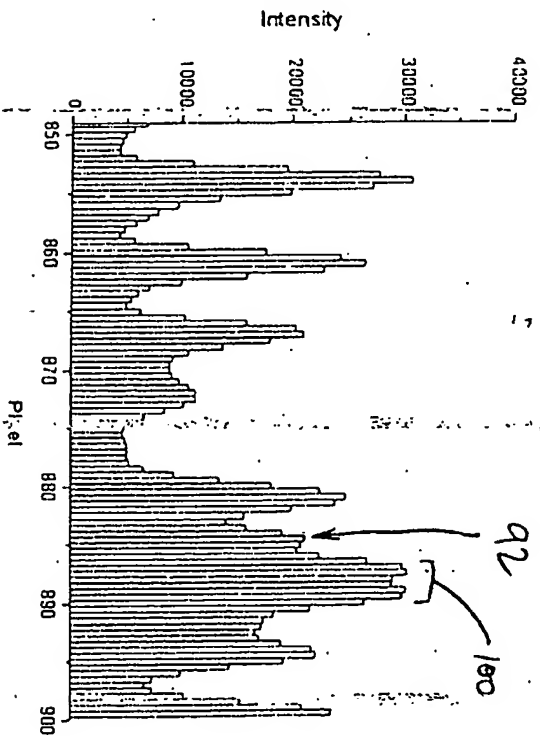
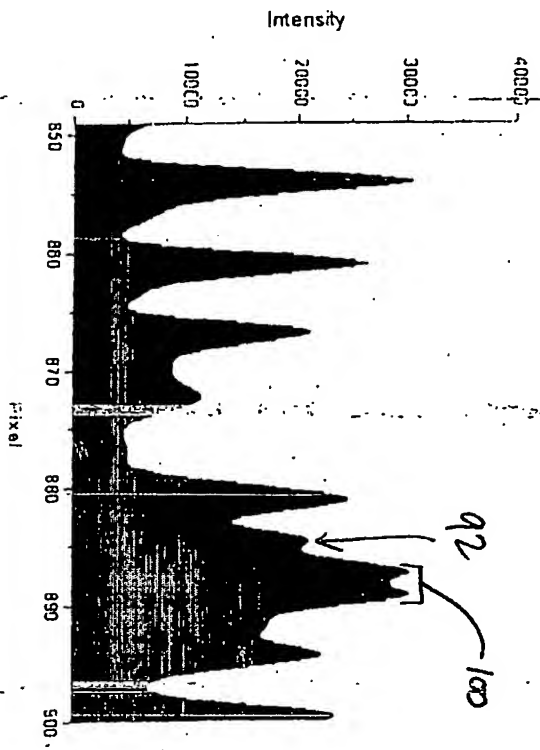


Fig 8



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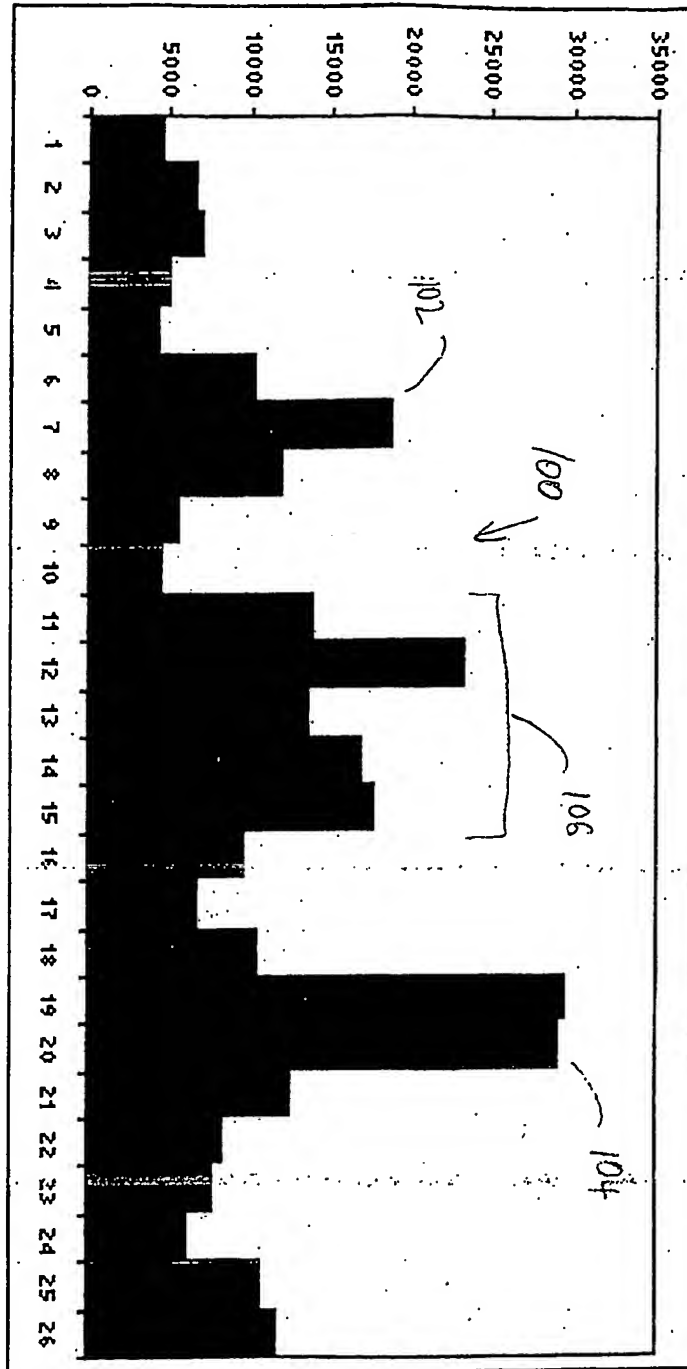


Fig 9

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Fig 10

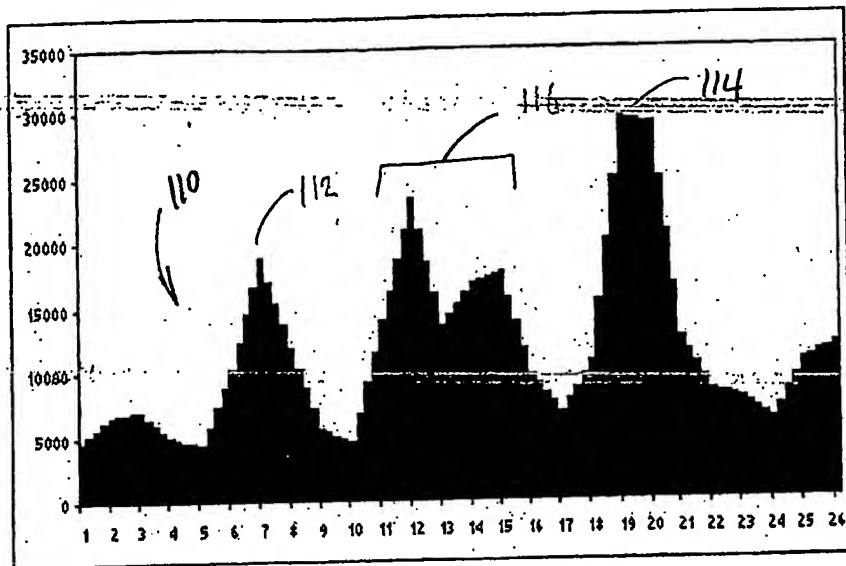
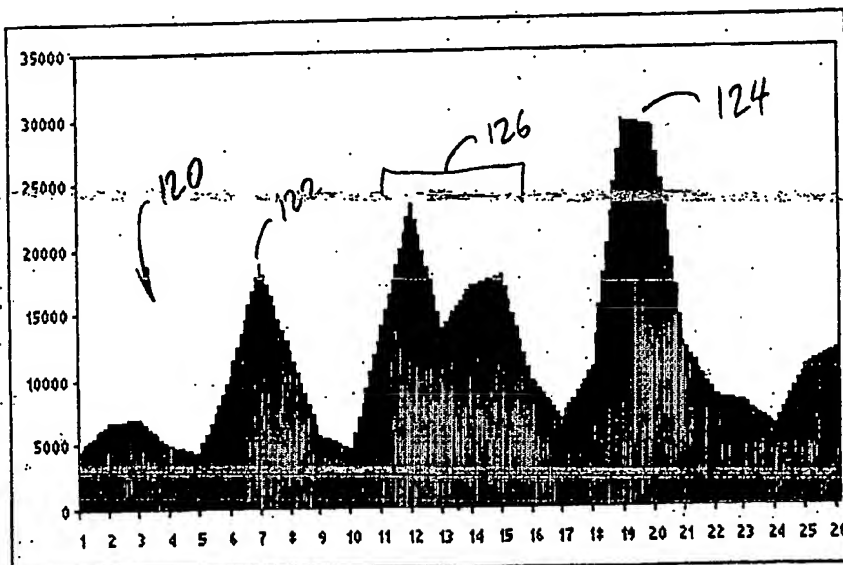


Fig 11



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Fig 12

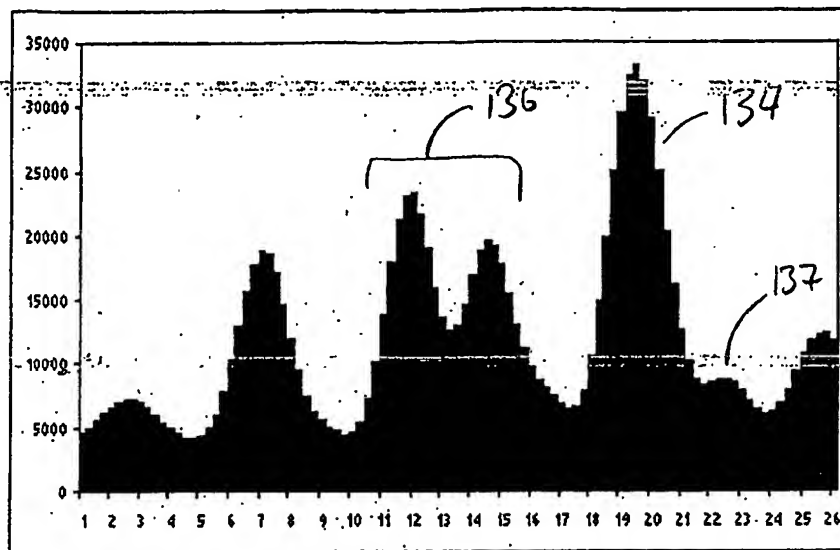
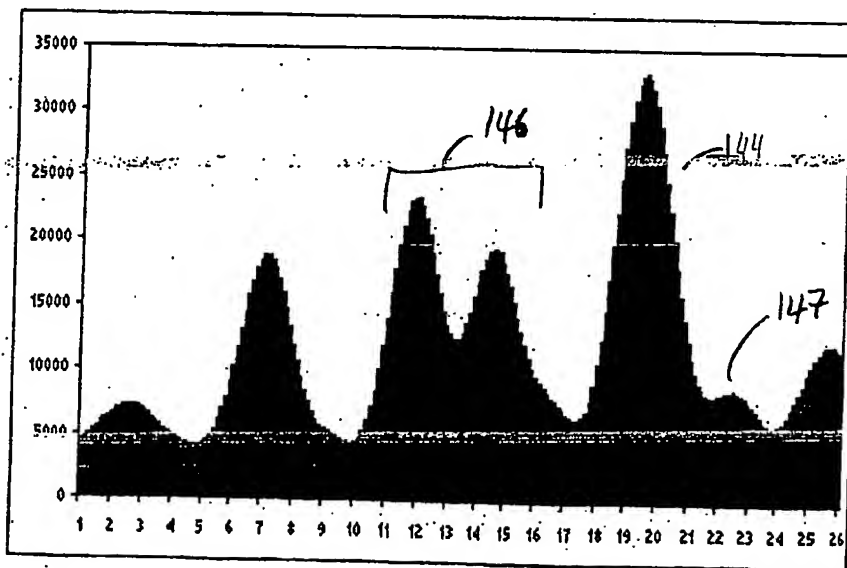


Fig 13



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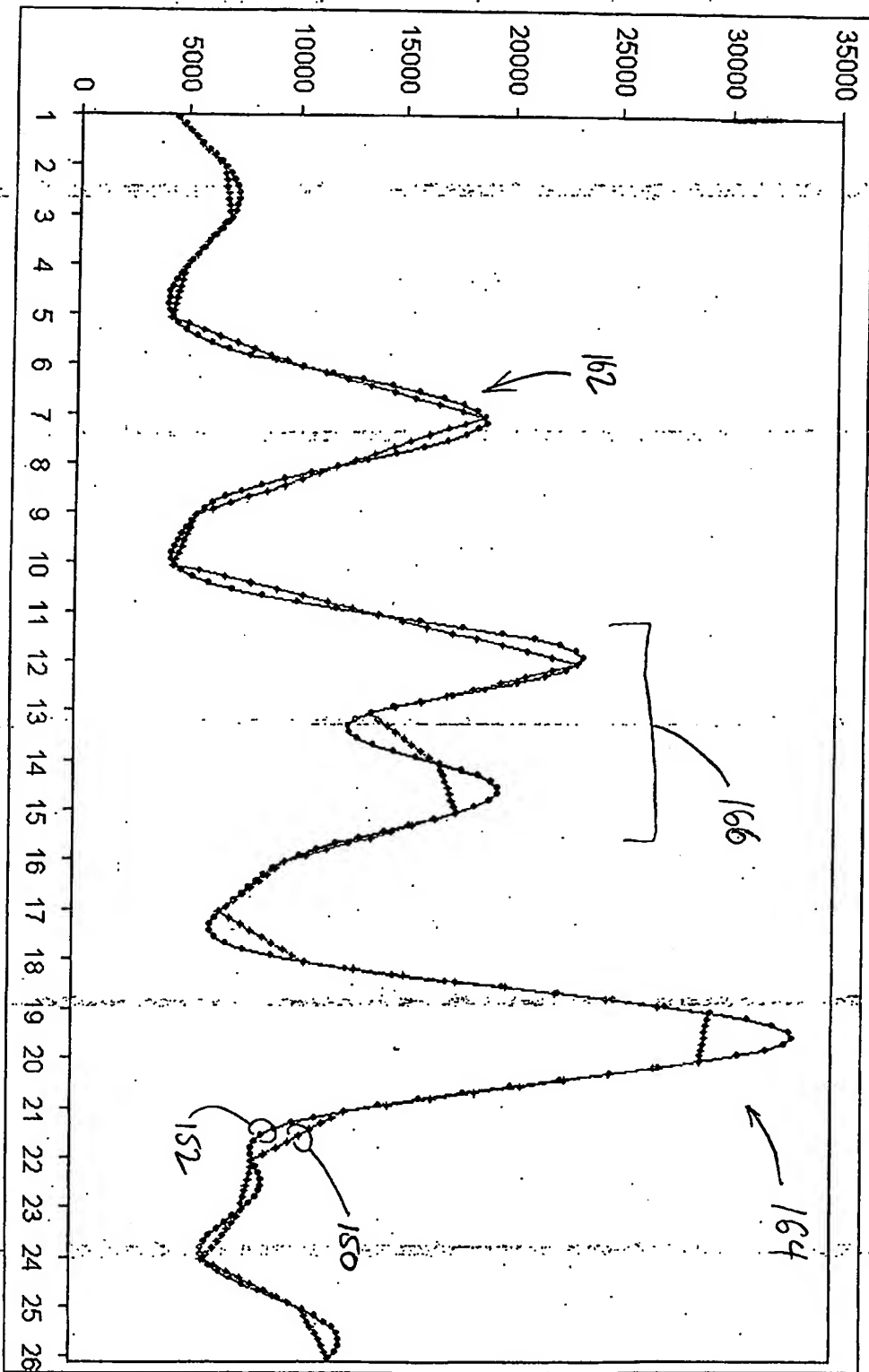


Fig 14

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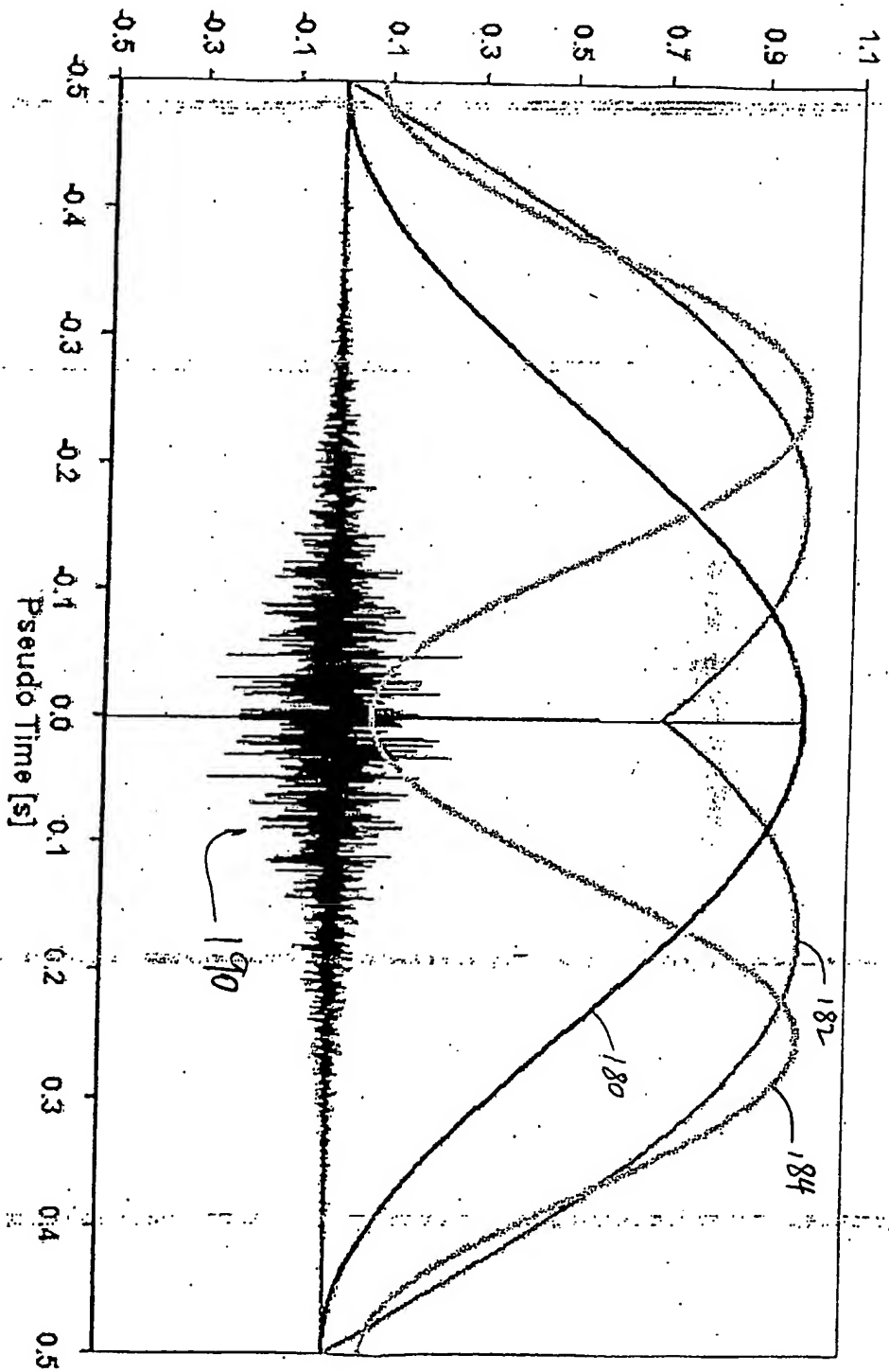


Fig 15.



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